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Evaluation of Hydrocarbon Measurement Techniques in Class B Fire Environments

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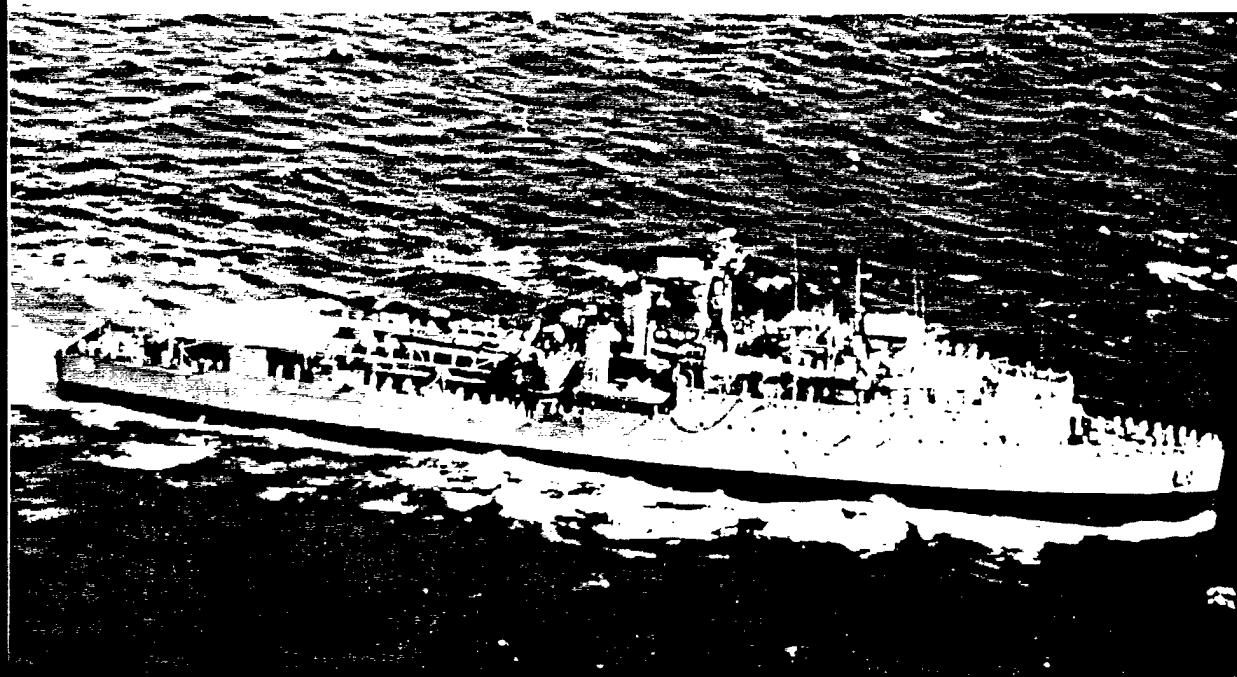
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13. ABSTRACT (Maximum 200 words) This report provides technical information for making baseline hydrocarbon measurements in a Class B fire scenario. The automotive industry along with the Environmental Protection Agency has expended a great deal of effort trying to measure reliably hydrocarbon emission from engines. These studies show a 20% error at concentrations less than 1000 ppm. The higher the hydrocarbon emission the greater the error. These hydrocarbons that would be typical of shipboard fire situations. To date no reliable technique has been identified for measuring the propensity of a post fire environment for reflash when air is reintroduced.				
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EVALUATION OF HYDROCARBON MEASUREMENT TECHNIQUES IN CLASS B FIRE ENVIRONMENTS

1.0 INTRODUCTION

In the event of a Class B fire onboard a surface ship or submarine, hydrocarbon (combustible gas) concentration measurements can be valuable to Navy firefighters. By knowing this concentration, the firefighters can determine the flammability of the environment and modify firefighting tactics accordingly. Without this knowledge, the attack of the fire space will be conservative and a potential for explosion may exist.

Recent attempts to validate Non-Developmental Items (NDI) hand-held multi-gas analyzers for hydrocarbon (HC) measurements in Class B fire atmospheres have shown the difficulty in obtaining good baseline hydrocarbon concentration measurements in these scenarios [1,2]. Results from the tests discussed in Reference 2 showed a large amount of scatter in these concentrations for samples taken concurrently. Furthermore, background samples of ambient air contained suspiciously high levels of hydrocarbons. In some cases, these concentrations were higher than those measured during the fire tests. It is suspected that some error was caused by sample contamination from residual hydrocarbons in previous samples.

Unburned HC concentrations resulting from Class B combustion, such as diesel fuel, are inherently difficult to measure. Problems are caused by the presence of high molecular weight hydrocarbons, large amounts of particulates, and water. High molecular weight hydrocarbons are problematic because of their low vapor pressures. Table 1 shows this trend by presenting boiling point temperature data at 1 atm for some hydrocarbons which have been identified in diesel engine

exhaust [3]. Since hydrocarbon's boiling points increase with increasing carbon number the higher molecular weight HCs are much more sensitive to sampling conditions than lighter molecular weight HCs, particularly those which are gaseous at ambient conditions (25°C at 1 atm). If the higher molecular weight hydrocarbons are present in high enough concentrations in the high temperature fire environment, they can condense out in the sampling system unless the sample is heated. This temperature is dependent on the concentration (or partial pressure) of a particular hydrocarbon in the mixture. To further demonstrate this problem, a typical distillation curve is provided in Figure 1. The data shown on the graph are based on Phillips number 2 diesel fuel [4]. This graph shows that the main hydrocarbon constituents of diesel fuel are approximately C₁₀ and higher since it begins to vaporize at about 220°C. Based on the temperature where 90% of the fuel is vaporized, the components reach carbon numbers as high as C₁₉.

Table 1. Hydrocarbons Identified in Diesel Engine Exhaust

Compound	Molecular Formula	Boiling Point at 1 atm (C)
methane	CH ₄	-162
ethane	C ₂ H ₆	-89
propane	C ₃ H ₈	-42
pentane	C ₅ H ₁₂	36
benzene	C ₆ H ₆	80
toluene	C ₇ H ₈	111
nonane	C ₉ H ₂₀	151
decane	C ₁₀ H ₂₂	174
naphthalene	C ₁₀ H ₈	218
dodecane	C ₁₂ H ₂₆	216

Another problem associated with Class B fires is that there can be a high level of soot (or particulates) formed. This is especially true for diesel fuel combustion. Soot is undesirable

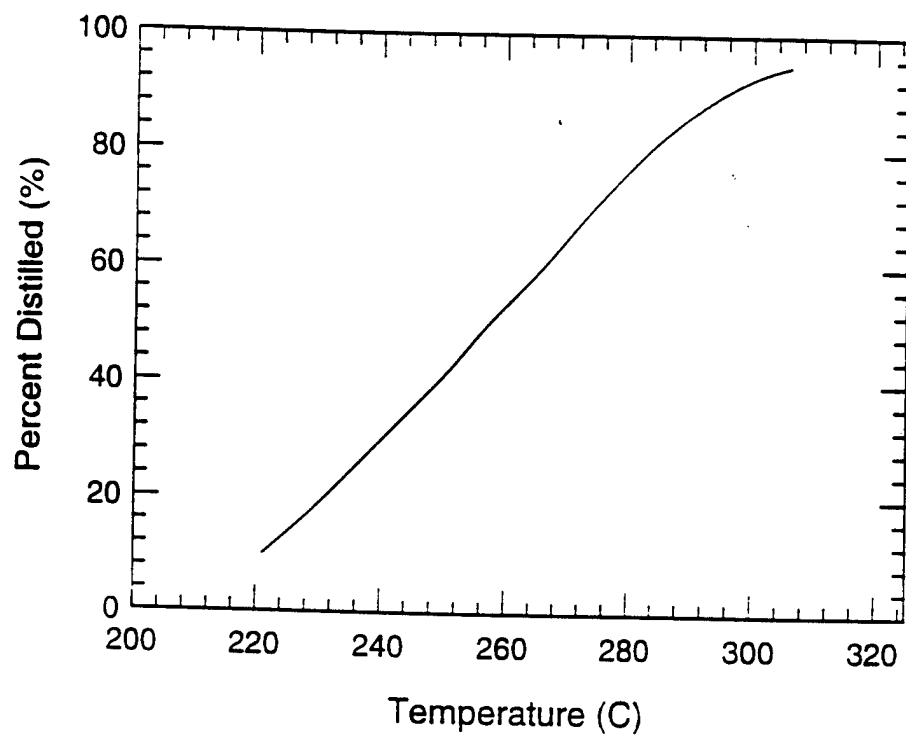


Fig. 1 - Typical No. 2 Diesel distillation curve [4]

since it tends to clog sampling systems and absorbs hydrocarbons. If the sample is filtered prior to analysis, there is a risk of filtering out some hydrocarbons if the filter is not heated sufficiently. The possibility of high concentrations of water is also of concern. Water concentrations as high as 15% by volume may exist in the fire effluent.

These parameters require that careful attention be paid to sampling, analysis, and calibration techniques. Each of these issues should be considered separately because if any one of these procedures is done improperly, the results may be erroneous.

An additional challenge with Class B fires is that HCs may be present in both the liquid (aerosol) and gas phase. This is a greater concern for underventilated fires (i.e., fuel-to-air ratio is greater than the stoichiometric fuel-to-air ratio) and for spray fires. By definition, there is not enough air available to oxidize all of the hydrocarbons in an underventilated fire; therefore, the concentration of unburned hydrocarbons will be higher than for well-ventilated fires. It is possible that some hydrocarbons will condense even in the fire compartment once they reach a cooler region. In addition, spray fires can allow unburned volatilized fuel to enter the exhaust stream. Ideally, one would want to measure the liquid phase hydrocarbons also since they can contribute to an explosive condition.

At a minimum, there is a need to be able to make reliable total hydrocarbon concentration measurements of sooty Class B combustion environments. This is necessary so that an experimental baseline can be established for the purpose of evaluating existing combustible gas detectors and providing a key research parameter.

2.0 OBJECTIVE

The objective of this study was to provide a summary and analysis of current techniques for hydrocarbon concentration measurements and to provide a recommended technique for use in making baseline hydrocarbon measurements in Class B fire environments.

3.0 APPROACH

Few fire researchers have published data in which reliable measurements of total hydrocarbon concentrations are presented. As a result, this study was aimed more toward techniques used by the EPA and in the automotive industry. A literature search was conducted by using key words such as emissions, exhaust gas measurement, and diesel exhaust. More emphasis was placed on evaluation of techniques related to diesel exhaust sampling since this is a more prevalent combustion fuel on Navy ships and is more difficult to analyze in comparison to lighter molecular weight hydrocarbon fuels (i.e., gasoline and alternative fuels). In addition, people from appropriate industries and academia were consulted to gain more insight into this problem. These researchers include personnel at the EPA, NIST, Princeton University, Drexel University, Horiba Instruments, Rosemount Analytical, and several commercial laboratories.

This report will first discuss the different hydrocarbon sampling techniques and their advantages and disadvantages. An explanation of the primary measurement devices used for hydrocarbon quantification will then be provided. Their advantages and disadvantages will also be discussed. Section 6.0 will present an overview of Class B fire research studies where HC measurements were recorded. This is followed by an explanation of federal standards for measuring the hydrocarbon emissions from both stationary and mobile sources. Some studies which have been conducted, primarily in the automotive community, are then explained. Methods for particulate measurement and considerations for instrument calibration will be discussed in Sections 9 and 10, respectively. The final section discusses the information presented and provides recommendations for making Class B fire measurements.

4.0 SAMPLING TECHNIQUES

It is important that proper sampling techniques are incorporated into a HC measurement test program. Improper sampling techniques can result in measurements which are meaningless. This section introduces the three techniques used for sampling hydrocarbons. These techniques include continuous, grab, and in situ sampling.

4.1 Continuous Sampling

Continuous sampling involves drawing a gas sample from the area of interest to an on-line measurement device. Generally, this is accomplished by using a pump to draw the sample through a length of tubing. The primary concern with this method is that HCs can condense out in the tubing prior to their quantification. In order to avoid this, the tubing should be heated. This can be done by wrapping the tubing with electrical heating tape or using tubing with a heated jacket. The desired temperature is dependent upon the hydrocarbon concentrations and the molecular weights. Generally, researchers heat sampling tubing to temperatures of 100°C or higher. However, heating the tubing does not eliminate the problems of soot clogging and contamination of the sampling system and detector. There is also the issue of catalytic activity of the heated metal in the air stream. Consequently, a filter is normally used in the sample line to avoid damage to the sample pump and obstruction of the small sample capillaries, which are typical of hydrocarbon analyzers. This will eliminate part of the soot problem, but it is still possible that soot will collect on the walls of the sample tube and cause some hydrocarbons to be adsorbed. An advantage of a continuous sampling method is that "real-time" measurements can be taken.

4.2 Grab Sampling

Grab sampling consists of drawing a gas sample into a container, such as a 1 liter stainless steel cylinder, so that it can be analyzed remote from the sampling location.

Theoretically, samples can be stored for indefinite periods of time before being analyzed provided there is no reactivity of the combustion products. One advantage of this method is that multiple samples can easily be obtained at the same time allowing for repeat analyses. This technique also provides more flexibility in taking multiple measurements throughout a test volume. Typically, the container is evacuated to ensure that there is no contamination from residual contents and so a sample may be drawn without a mechanical device. In order to eliminate the need for heated samples, it is a common practice to dilute the sample first. By diluting the sample, the partial pressure of the hydrocarbon species will be reduced. If this pressure is reduced far enough, the hydrocarbon will not condense out in the sample flask. Obviously, the amount of dilution required to achieve this will vary depending on the levels of hydrocarbons present in the sample. When diluting the sample, the amount of dilution must be measured so that the actual concentration can be calculated.

4.3 In Situ Sampling

In situ sampling is when gases are measured in place. In other words, there is no need for gas sample transport or collection. This type of sampling is the most ideal since one does not need to worry about condensation of water or hydrocarbons. However, in the case of a fire scenario, the measurement device must be robust enough to withstand the elevated temperatures and the presence of particulates. This method also allows for "real time" measurements to be acquired.

5.0 MEASUREMENT TECHNIQUES

A description of several types of instrumentation used to make HC concentration measurements is given in Reference 5. These instruments include the total hydrocarbon analyzer, gas chromatograph, Fourier Transform infrared spectrometer, and fiber optic sensor.

6.0 CLASS B FIRE RESEARCH STUDIES

As stated earlier, little work has been performed on making hydrocarbon measurements in fire scenarios. This section will present some Class B fire studies that have been conducted, beginning with those done on the *ex*-USS SHADWELL. Results from compartment fire experiments as well as hood experiments will also be discussed.

6.1 *Ex*-USS SHADWELL Experiments

As mentioned previously, hydrocarbon measurements in Class B fire environments have been attempted on two occasions [1,2]. In the second set of tests [2], unfiltered samples were acquired by drawing hot gas samples directly into stainless steel bottles (1.7 l). The samples were analyzed using a GC/FID in which the column had been bypassed. The injection system, which included the sample bottle, pressure gage, injection manifold, and injection loop, was not heated. The results of the analysis showed a large amount of scatter. In addition, analysis of bottles filled with "background" samples (taken prior to fire tests) showed that some contained higher concentrations of hydrocarbons than those measured during any of the fires. Several factors may have contributed to these problems. Drawing a sample with soot may lead to erratic results based on how it deposits within the bottle. This soot may trap out some of the hydrocarbons in the sample. Also, since the injection system was not heated, condensed hydrocarbons could have been trapped in these components. Several instrument checks suggested that the injection system may have been contaminated, in addition to, the system used to evacuate the sample bottles. Attempts were made to acquire diluted samples; however, those results also showed an unacceptable amount of scatter.

6.2 Other Class B Fire Experiments

Gottuk performed compartment fire experiments with hexane pan fires [6]. Total hydrocarbon concentrations were measured using a hot FID which was located approximately

twenty feet from the sampling location. The tubing was heated to 130°C or higher using heating tape and the FID oven temperature was 105°C. Based on a carbon mass balance, measurement errors ranging from 4 to 30% carbon were reported for global equivalence ratios (i.e. fuel-to-air ratio normalized by the stoichiometric fuel-to-air ratio) ranging from 0.64 to 3 [6]. As would be expected, the error increased as the global equivalence ratio increased due to the resulting higher concentrations of hydrocarbons and, potentially, the presence of higher molecular weight hydrocarbons. Concentrations as high as 10% methane were measured for tests with equivalence ratios greater than 2.5.

Researchers at NIST have attempted to make HC measurements in hexane compartment fire experiments similar to those performed by Gottuk [7]. These measurements have been performed using a heated FID with heated sample lines. To date, they have been unsuccessful at obtaining reliable measurements. They have experienced problems due to high concentrations of water in the gas samples (the unit has a sample regulator which is not in the oven) and equipment failure due to corrosion. Corrosion was most likely caused by acidic water, but this was not verified.

Several researchers have reported HC measurements from hood experiments. Beyler performed hood experiments with both gaseous and liquid fuels (propane, propene, hexane, toluene, methanol, ethanol, isopropanol, and acetone) [8]. Hydrocarbons were measured as methane equivalents, using a GC with a FID modified for use as a total hydrocarbon analyzer. The THC analyzer was heated to 85°C as were the sample lines. In general, equivalence ratios as high as 1.4 were studied with corresponding hydrocarbon measurements ranging from about 5 to 7.8%. There was typically a distinct trend of increasing carbon error with an increase in equivalence ratio and subsequently higher hydrocarbon concentrations. The carbon error represents the amount of carbon unaccounted for in CO, CO₂, and total hydrocarbon measurements. This error is attributed primarily to errors in the THC measurement. Beyler observed errors as high as about 25% for toluene (a common component in gasoline and diesel fuel), 16% for propene and methanol, and about 12% for acetone, isopropanol, and propane.

These results are consistent with those of Gottuk who observed carbon errors of about 17% for an equivalence ratio of 1.7 (HC concentration was 4% methane).

Toner [9] and Morehart [10] also performed hood experiments. In the experiments conducted by Toner, natural gas was burned and measured with a GC which had a thermal conductivity detector [9]. The HC species which were measured included methane (CH_4), ethylene (C_2H_4), ethane (C_2H_6), and acetylene (C_2H_2). The GC oven was heated to 65°C as was the sample probe from the hood. Ethylene, ethane, and acetylene were measured only in small quantities in rich flames. At equivalence ratios around 1.5 to 2, concentrations of 5% and 0.6% were measured for methane and the C_2 hydrocarbons, respectively. Morehart reported similar results in his hood experiments [10]. These tests used a wider range of gaseous fuels.

This research shows an increase in measurement error with an increase in equivalence ratio, particularly for fuel-rich conditions. Furthermore, all fuels tested had low molecular weights in comparison to diesel fuel and considerable measurement errors were still reported. Despite these problems, researchers were able to measure hydrocarbon concentrations which were above the LEL. It is important to emphasize that no studies were identified where higher molecular weight hydrocarbon fuels, such as diesel fuel, were burned.

7.0 FEDERAL TEST PROCEDURES

The United States Government has established test procedures for measuring emissions from both stationary and mobile sources. This section summarizes these methods.

7.1 Stationary Source Procedure

The Environmental Protection Agency's (EPA) Method 25 Determination of Total Gaseous Nonmethane Organic Emissions as Carbon is a specification used to determine the volatile organic compounds (VOC) in emissions from stationary sources (such as generators and

boilers) [11]. The basic technique is to first oxidize all nonmethane hydrocarbons to carbon dioxide (CO_2), then convert it to methane and measure the resulting concentration using an FID. One advantage with this technique is that all measurements are of the same hydrocarbon species so that there is no need to consider FID response factors.

The sampling system has several components; heated probe, heated filter, condensate trap, flow control system, and sample tank (Figure 2). The probe must be heated to maintain a gas temperature of 129°C and the filter must be heated such that the gas temperature is at least 121°C . A U-tube packed with quartz wool is specified for the condensate trap. This trap is placed in a dewar packed with dry ice. The sample is collected in a sample tank with a volume at least 4 l and is constructed of stainless steel (SS) or aluminum.

The condensate recovery apparatus is comprised of a heat source, oxidation catalyst, nondispersive infrared (NDIR) analyzer and an intermediate collection vessel (Figure 3). The heat source is used to heat the trap to 200°C . In order to oxidize the organics from the condensate trap, the sample is sent through tubing packed with chromia or alumina pellets and mounted in a 650°C tube furnace. The NDIR analyzer is used to monitor the combustion progress by monitoring the CO_2 concentration. A flow control valve keeps the system near atmospheric pressure. The sample is collected in a vessel (SS or aluminum) with a volume of at least 6 liters.

The nonmethane organic compounds (NMO) analyzer consists of a GC capable of NMO analysis by backflushing, an oxidation catalyst, reduction catalyst and an FID (Figure 4). The oxidation catalyst is the same as described above in the condensate recovery apparatus. The reduction catalyst is a tube packed with nickel powder which is mounted in a 400°C furnace. The separation column is a tube packed with 60/80 mesh Unibeads 1S followed by a tube packed with 60/80 mesh Carbosieve G. The linearity of the FID must be verified over their specified range.

Calibration of this system involves 13 calibration gases. Three concentrations of propane are used to verify the FID linearity. The NDIR analyzer is calibrated with 3 calibration gases in addition

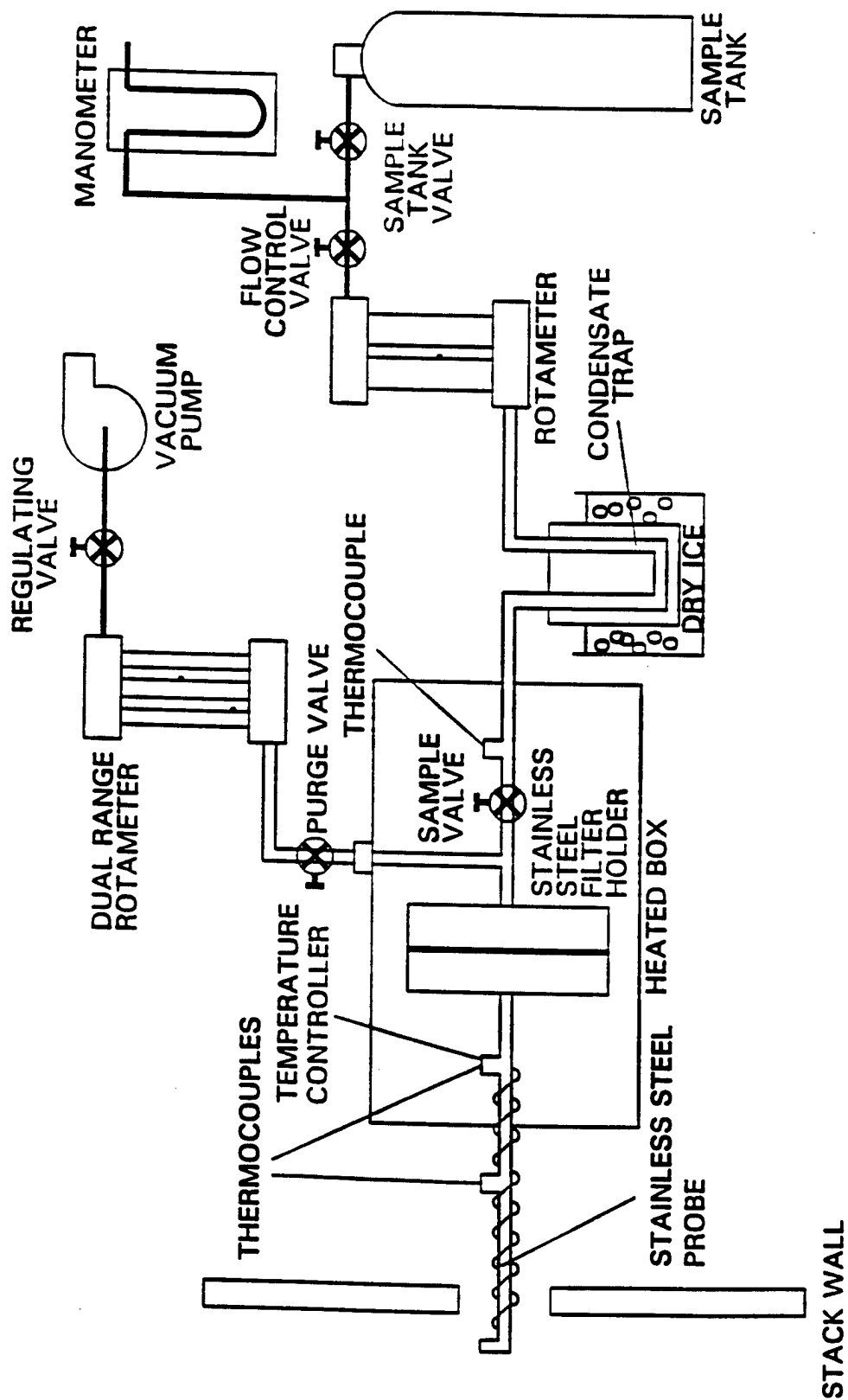


Fig. 2 - Sampling train as specified by EPA Method 25 (taken from EPA Method 25 [11])

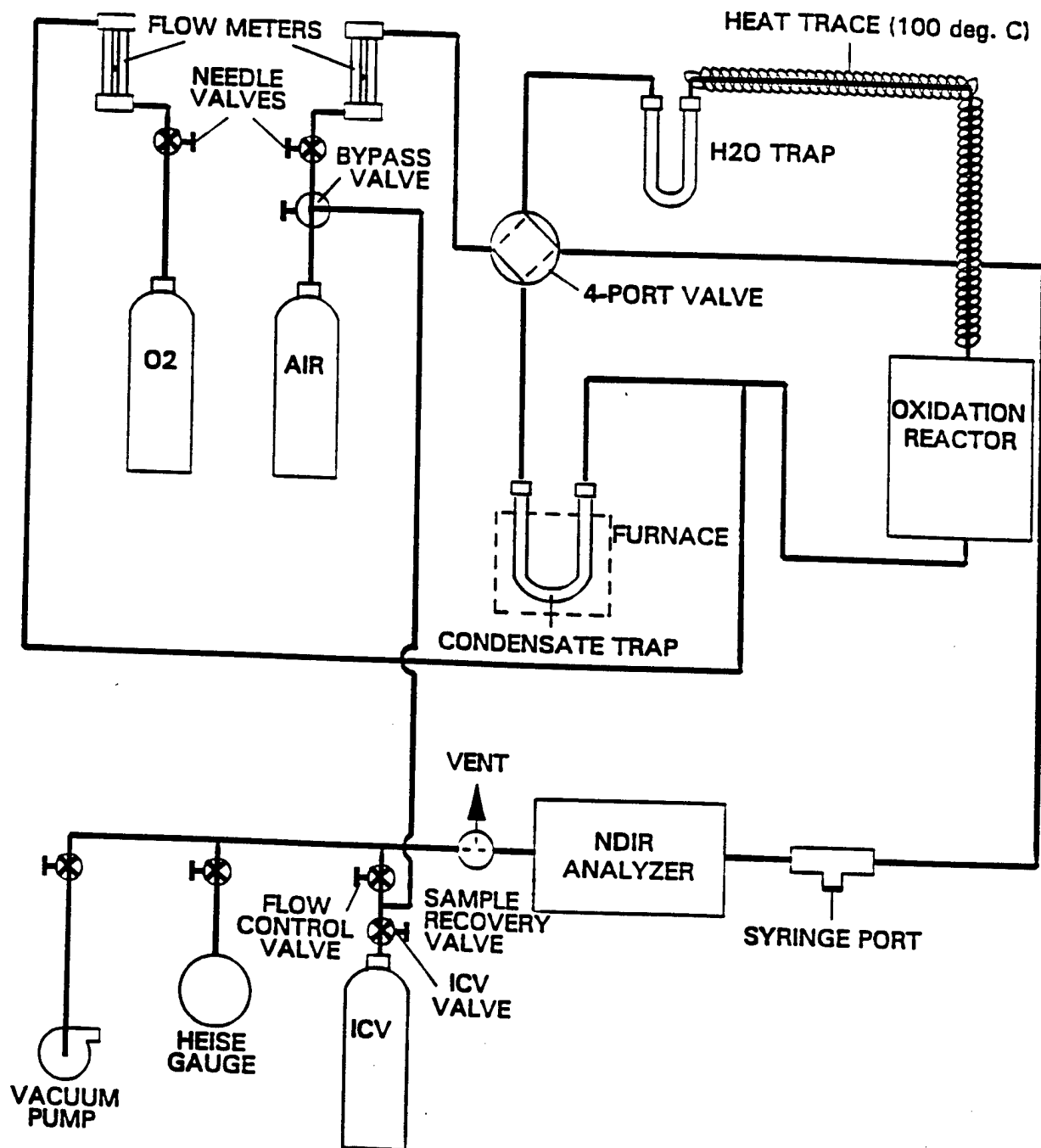


Fig. 3 - Condensate recovery system as specified by EPA Method 25
(taken from EPA Method 25 [11])

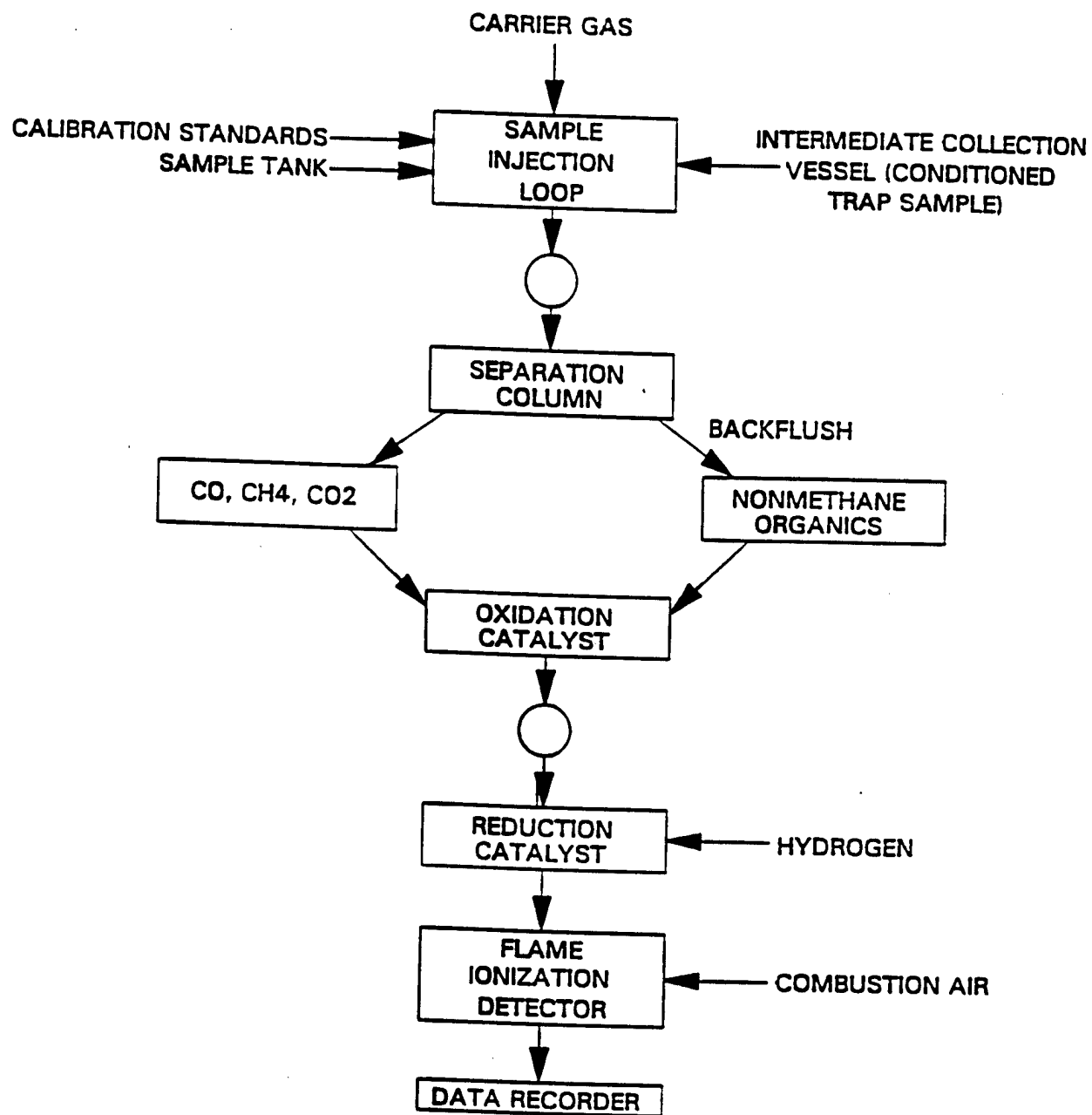


Fig. 4 - Simplified schematic of nonmethane organic (NMO) analyzer
(taken from EPA Method 25 [11])

to nitrogen. The NMO system is checked with 4 different hydrocarbon species, 3 of which are at one concentration and the other at 4 different concentrations.

This method is approximately 15 years old. The EPA is reportedly trying to develop a better technique using FTIR spectroscopy [12]. No further details of this were available.

7.2 Mobile Source Procedure

The Federal Test Procedure provides specifications for measuring emissions from mobile diesel engines such as cars and trucks [13]. Mass emissions of hydrocarbons, carbon monoxide, carbon dioxide, nitrogen oxide, and particulates are measured. Exhaust gas is generated using a dynamometer with an engine running on the regulation fuel. Exhaust gas sampling is done by first diluting the sample using constant volume sampling (CVS). Samples are diluted in order to reduce the partial pressure of the hydrocarbon and water constituents such that no condensation will occur at room temperatures. There are three methods which can be used to dilute the sample. These methods include using a Positive Displacement Pump Constant Volume Sampler (PDP-CVS), a Critical Flow Venturi Constant Volume Sample (CFV-CVS), or an Electronic Flow Control Critical Flow Venturi Constant Volume Sampler (EFC-CFV-CVS). The CVS flow rate must be large enough to ensure that condensation will not take place.

A sample probe is located downstream of the dilution tunnel for continuous monitoring of HCs and nitrogen oxides. This sample line is heated to $191 \pm 11^{\circ}\text{C}$ and hydrocarbons are measured with a heated FID which is operated at a temperature of $195\text{-}197^{\circ}\text{C}$. The analyzer is calibrated using propane and the fuel for the flame is specified as 40% H_2 and 60% He. In addition, bag samples are taken and analyzed for carbon monoxide, carbon dioxide, nitrogen oxide and hydrocarbons. Again, a heated FID is used for the hydrocarbon analysis. Particulates are measured by running the dilute exhaust through 1 or 2 filters over the period of the test. The filters are either fluorocarbon-coated glass fiber filters or fluorocarbon-based (membrane) filters with a minimum diameter of 70 mm. The mass emission rate is determined by weighing the filters.

8.0 AUTOMOTIVE RESEARCH PROGRAM STUDIES

There have been two substantial research efforts headed by the Coordinating Research Council (CRC) and the Auto/Oil Air Quality Improvement Research Program (AQIRP) to develop reliable hydrocarbon emissions measurement techniques. These studies will be discussed as well as further emissions studies.

8.1 Coordinating Research Council

The Coordinating Research Council, Inc., is a non-profit organization that coordinates research efforts that pertain to engineering and environmental studies involving automotive equipment and petroleum products. Sustaining members include the American Petroleum Institute (API), Society of Automotive Engineers (SAE) and U.S. Car. By coordinating efforts, personnel in these organizations can collaborate together and with the Government. Since the CRC has no research facilities, two approaches are taken to conduct studies. The first is a large-scale research program that exceeds what any one company could undertake. The second approach involves supporting research that is contracted out to universities and other research organizations. Council funding is primarily provided by API, the American Automobile Manufacturers Association, and the Government.

In 1967, the Air Pollution Research Advisory Committee (APRAC) of the CRC began cooperative work to evaluate methods for measuring the total hydrocarbon concentrations in diesel exhaust. Their primary goal was to determine how good the inter-laboratory agreement was for hydrocarbon analysis. In the first and second phase of this effort, thirteen laboratories participated in quantifying the emissions from a diesel engine at three load settings [14]. All laboratories used an identical engine and number 2 diesel fuel that was from the same batch. During Phase I, the only instructions given to each participant were the load settings to test (idle, mid-power and high-power) and the fuel to use. Each laboratory determined what measurement technique to use. The results of this effort were an unexplained wide scatter in the data. Some measurements varied from

the median values by as much as 50% relative. Therefore, a second phase was conducted in which the APRAC provided more specific instructions to the participants, in hopes of obtaining more consistent data.

In the second phase, the test matrix was dictated including the days in which each test was to be performed (to determine errors day-to-day). Also, a small mixing tank was added in the exhaust line from the engine and the sample line was heated. The sample line temperature was not specified. Thermocouples were placed before and after the mixing tank as well as in the center of the sample line. The results from these tests showed better relative agreement than Phase I results. The amount of improvement was not explicitly stated. Hydrocarbon concentrations measured in both phases typically ranged between 50 and 300 ppm.

In Phase I, 3 labs used GC/FIDs and others used continuous THC analyzers that also incorporated FIDs. During Phase II, 2 participants used GC/FIDs, 1 used both a GC and FID, and the rest used continuous THC analyzers. Although there was an improvement between Phase I and II, the data was not repeatable enough to conclude whether the GC data was significantly different from the continuous THC data. Some laboratories determined that oxygen was important in their analysis and corrected for this effect while others did not report any problems with it.

In response to the poor measurement agreement among laboratories, Phase III of this effort was conducted [15]. In these tests, the hydrocarbon levels from the exhaust of one engine were measured with 12 hydrocarbon analyzers. Each participating laboratory provided their own instrument and installed it at this central location. While any type of instrument was welcomed, all participants used continuous THC analyzers and each chose a mixture of propane in either air or nitrogen as a calibration gas. Three sets of tests were conducted, all with satisfactory agreement between analyzers. In the first two sets of tests, engine operating conditions were varied. Measurement errors for each of the individual analyzers were $\pm 3\%$ relative for both span and exhaust gases. The errors were higher though when average readings were compared among the different analyzers; for calibration gases it was $\pm 10\%$ and for exhaust samples $\pm 12\%$ relative. The

improvement of readings between laboratories, with respect to Phase I and II results, was attributed partially to the collaboration that existed between participants and are considered to be biased to some degree.

The third set of tests in Phase III involved injecting a known amount of either heptane, hexadecane, or 1-methyl naphthalene into the exhaust pipe. Instrument response for heptane was generally 100% while for n-cetane and 1-methyl naphthalene, the average response was 85% of the amount injected. Therefore, for this range of concentrations, this suggests that in the boiling range of diesel fuel (aromatics C_{11} or C_{12} and parafins C_{12} - C_{20}), the FID response will be 80-90% of those in the C_3 - C_7 range.

After achieving promising results in Phase III, Phase IV was initiated to determine if the inter-laboratory reliability had improved from that observed in Phases I & II [16]. Fifteen laboratories participated in these tests; each one had an identical multi-cylinder engine that was used to generate exhaust samples. All laboratories used the same sampling procedure (heated FID with heated sample lines from the engine exhaust pipe). As in other phases, each laboratory was also sent 2 bottles of calibration gas to analyze. A specified test procedure and schedule was followed. While Phase II and III results were probably biased due to communication between participants, it is believed these measurements were truly independent. Again variations between exhaust samples were greater than for calibration gases. The average error within each laboratory was 3% relative for calibration bottles and 10% relative for exhaust samples. When comparing the grand averages among the laboratories, the error increased to 10% for calibration bottles and 22% for exhaust samples. As in Phases I and II, it was determined that these large differences could not be due solely to variations in the engines. The main source of error was considered to be the measurement techniques. It should be noted that one laboratory reported a low sample line temperature and that they consistently reported low hydrocarbon values. This emphasizes the importance of the heated sample lines and the measurement errors that can be introduced when the line temperature is not constant from one test to another, or from one laboratory to another.

8.2 Auto/Oil Air Quality Improvement Research Program

The Auto/Oil Air Quality Improvement Research Program (AQIRP) is a cooperative research program begun in 1989 with three domestic automobile companies and 14 petroleum companies. The purpose of the program is to develop data that is related to possible improvements in air quality and vehicle emissions. This improvement may result from reformulated gasoline and alternative fuels as well as advances in automotive technology.

In the first phase of the program, a technique for measuring the hydrocarbon and ether emissions from gasoline and alternative fueled engines was developed [17]. Thirty four vehicles were tested using 24 reformulated gasolines and 2 reference gasolines. In addition, there were 19 flexible-fuels and variable-fueled vehicles that were run on 2 methanol/gasoline blends and industry average gasoline. Three types of emissions were measured: tailpipe, evaporative and running loss.

Exhaust samples were taken in Tedlar bags. Tailpipe samples consisted of dilute tailpipe emissions. For gasoline tests, samples were diluted by 15/1 and for methanol by 30/1. Evaporative emissions samples were taken inside the test chamber to measure the evaporation of hydrocarbons from non-combustion sources. Evaporative fuel loss under simulated driving conditions was measured with the running loss samples.

These samples were analyzed using a GC/FID, with a single column, to measure 140 hydrocarbons from C_1 to C_{12} including paraffins, olefins, aromatics, and ethers. The bag samples were not heated, however, the sample valve and sample loop were heated to 120°C and lines were shortened where possible to help minimize hydrocarbon losses. In order to tabulate total hydrocarbon emissions, the response factor was assumed to be 1 for all nonmethane hydrocarbons. This assumption was based on earlier studies which showed that these response factors ranged between 6 and 8 %. The analysis required 54 minutes and the system had a detection limit of 0.05 ppm C_1 . Typical concentrations of non-methane hydrocarbons measured in this study were less

than 50 ppm C_1 . Calibration was performed daily with a mixture containing 21 components which consisted of normal alkanes (C_1 to C_{12}) and other compounds.

Several noteworthy problems were mentioned. In early tests, high boiling end hydrocarbons were being trapped in the sample valve and sample loop inlet. As a result, these lines were insulated and heated as mentioned earlier. In addition, the injection system was baked for one hour every day at 240°C . Another problem was that the column degraded quickly despite baking it daily. This was solved by washing the column with methylene chloride. Eventually, a pre-column was added, which was disposed of several times while testing.

Results showed that hydrocarbon losses were minimal. The concentrations obtained with GC analysis were used to calculate the total HC measurement by taking into account the species known not to have response factors of 1 (methane, MTBE, ETBE, formaldehyde, acetaldehyde, methanol and ethanol). This concentration was compared to the value obtained from a benchtop FID that was located at the point where the grab samples were taken. For the 1989 vehicles, the diluted sample concentrations were an average of 11% lower than those concentrations measured with the bench top FID. For the 1983-85 vehicles, this error was an average of 1.4% relative. Furthermore, the 140 species generally accounted for 93% of the total emission mass for both old and new engines. There was a strong correlation between the amount of unidentified compounds and the T90 (90% distillation temperature) volatility level of the fuel, thus implying that more emphasis was needed on higher molecular weight characterization (C_{10} - C_{12}).

In Phase II of this research, the hydrocarbon species library was increased from 140 to 154 species [18]. The main additions to the library consisted of aromatics in the C_{10} - C_{12} range. Also, the single column technique was expanded to 2 columns in order to better quantify these additions. The first of these columns measured HCs in the C_1 - C_4 range and the second in the C_4 - C_{12} range. The percentage of THC mass which could be accounted for in the typical exhaust sample increased from 93% to $95\pm 3\%$. Analysis times remained under one hour. The range of HC measurements

obtained in Phase II were not included. However, since the experiments were very similar, it is assumed that they were similar to those obtained in Phase I.

Despite the complexity of the hydrocarbon identification and quantification, this technique is promising particularly when one considers that 95% of the total carbon mass could be determined. However, no tests were conducted with diesel fuel. As a result, the library may be insufficient for higher molecular weight hydrocarbon measurements.

A further review of literature and conversations with professionals in industry and academia revealed that most HC measurement techniques follow the same principles of those mentioned above (direct FID or GC/FID). In many cases, the samples are diluted and the sample lines are heated.

8.3 Other Related Studies

Many studies have been documented on the measurement of hydrocarbons in automotive exhaust, some of which pertain specifically to diesel exhaust [3,19-22]. Most of these follow the same basic procedure in that the exhaust sample is diluted, collected, and analyzed on a GC/FID. The GC separation techniques have improved dramatically over the years, both by the number of runs needed to analyze a sample and the number of species that can be measured. For example, one early study only measured C_2 - C_6 hydrocarbons [19]. In a later study by the CRC, 4 stages were needed to analyze C_1 - C_{10} hydrocarbons [20]. A more recent technique described by Rudlein, et al., proposes a single run technique for C_2 - C_{12} quantification. Regardless of the types of species being measured, the importance of heating exhaust sampling has been recognized [3,19]. Yamane, et al., used a heated syringe to collect the exhaust sample and noted that the temperature of the syringe had a dramatic effect on measurements especially those above C_6 [3].

In a study conducted by Koike, et al., two different sampling techniques are presented in which the sample is condensed [21]. These methods are compared to the conventional sampling

method. The first of these alternative methods was the Cold Trap Injection (CTI) Method. A sample is concentrated by cooling and condensing it with liquid nitrogen. In order to analyze the sample, it is heated to desorb the hydrocarbon species and the concentrations are measured using a GC. The authors did not specify the heating conditions (i.e., temperature and amount of time heated). The second method was the Tenax Cold Trap (TCT) Injection. With this method, the sample is passed through a tube packed with Tenax absorbent where the hydrocarbon species are adsorbed and concentrated. The tube is then heated as a carrier gas is passed through it. The hydrocarbon species are desorbed and collected in a cold trap (cooled to -120°C). This trap is then heated prior to GC analysis in order to desorb the hydrocarbons. Analysis for $\text{C}_2\text{-C}_{12}$ showed generally good agreement between the 3 methods. The CTI method did show some problems detecting hydrocarbons in the $\text{C}_2\text{-C}_4$ range.

Due to the amount of room required for a full tunnel and the expense involved, a common modification to the Federal Test Procedure is to use a "mini-dilution" tunnel for diluting exhaust samples. Some of these studies have been documented [23-26]. Researchers have gone through extensive testing to ensure that this system will give the same results as the method prescribed in the Federal Test Procedure. In most of the studies reviewed, agreement between small and full scale dilution tunnels was generally noted within 10%.

At Princeton University, Dryer and his research group have been performing hydrocarbon measurements of exhaust samples from an atmospheric flow reactor for a number of years [27]. Their current technique is to collect exhaust samples through lines heated to at least 100°C . These samples are drawn directly into tubes which are housed in an oven which is also heated to 100°C . They are then stored in this oven until they are analyzed. The analysis system consists of a GC with 2 columns and a thermal conductivity detector. The injection system is also heated to 100°C so from the time of exhaust gas generation to the time of analysis, the temperature of the sample never drops below this value. One sample requires about an hour to run through the two GC columns and hydrocarbons up to C_{12} have been measured. As their techniques have progressed, they have moved from gaseous to liquid fuels. Early testing was with methane while current testing includes

octane. Using current test results to perform carbon balances between the exhaust products measured and the amount of fuel injected, measurement errors are generally less than $\pm 10\%$.

As mentioned earlier, the use of FTIR spectroscopy in hydrocarbon analysis has been researched for at least a decade. In several studies, low molecular weight hydrocarbons have been measured in exhaust samples [28-30]. However, the individual identification of higher molecular weight compounds was not possible. This is because lighter molecular weight HCs have strong, sharp absorbance bands whereas heavier HCs lose their distinctiveness [28].

Herget, et al., measured the hydrocarbon content from automobile exhaust (the fuel is not specified) using an FTIR [29]. They observed resolved line spectra for hydrocarbons with low carbon numbers (C_1 and C_2), but observed a continuous absorbance in the region of 2800 to 3200 cm^{-1} , which represented the higher molecular weight hydrocarbons. The aliphatics were clustered around 2950 cm^{-1} while the aromatics were clustered around 3100 cm^{-1} . An integrative approach was used to quantify the total hydrocarbon concentration in this region. Since it was a preliminary study, no specifics were provided as to how well this approach works.

In a study by Roberts and Lowry, both raw and dilute samples were analyzed from engine exhaust fueled by gasoline and alternative fuels [28]. They were able to quantify twelve hydrocarbon species, some of which were compared with FID or GC/FID analyses. A comparison of some typical GC/FID and FTIR concentrations showed agreement within 5% for methane, ethene, acetylene, ethane, and propane. Propene had much worse agreement (greater than 100% relative); however, the concentrations were less than 1 ppm. They also reported difficulty in discriminating the aromatics due to interference from CO_2 and non-aromatic hydrocarbons. As an alternative to individual aromatic separation, the total aromatic HC concentration was calculated based on the benzene ring. In addition, identification of paraffins with more than 4 carbon atoms was problematic. This was bypassed by using a heavier hydrocarbon as a calibration standard and "estimating" the concentration in the actual sample based on this calibration. Unfortunately, more specific details regarding their techniques are not provided. Despite the trouble with individual

species measurements, total hydrocarbon measurements using the FTIR and FID compared to within 5%. It was noted that there was more difficulty analyzing the exhaust from gasoline than for alternative fuels and the FTIR/FID comparison results do not specify what types of fuels are compared. Total HC concentrations were on the order of 50 ppm which indicates that some of their quantification assumptions may not correspond to a large percentage of the total concentration.

A similar study by Shore and deVries was conducted in which seven HC species in engine exhaust were measured [30]. These hydrocarbons included methane, ethane, ethene, acetylene, propene, 1,3-butadiene, and formaldehyde. Good agreement was noted between their FTIR data and corresponding GC analyses for four of the seven hydrocarbons (ethene, acetylene, propene, and formaldehyde). The difference in readings ranged from no difference to 22%, however, most were less than 15%. Typical measurements reported ranged from 10 to 146 mg/mile for these species. Calibrations were performed with gas mixtures containing C₁-C₁₀ n-alkanes, C₂-C₁₀ 1-alkenes, C₂-C₄ 1-alkynes, C₄-C₆ substituted alkenes, C₄-C₈ substituted alkanes and C₆-C₉ aromatics. Based on this calibration data, it was proposed that methane was not measured accurately due to interference caused by higher molecular weight hydrocarbons. Also, calibration data indicated possible interference problems for ethane and propene. The authors suggest that adjustments to their FTIR software may eliminate some of these interference problems.

9.0 PARTICULATE MEASUREMENT

To this point, all techniques discussed have been for the analysis of gaseous phase hydrocarbons. There are actually two additional states of hydrocarbons in exhaust samples: semi-volatile organic compounds and particle bound hydrocarbons [25]. Gautam defines semi-volatile organic compounds (SOC) as compounds with vapor pressures between 74^{-2} and 74^{-9} torr at ambient temperatures. Black states that particle bound hydrocarbons are usually C₁₄-C₄₀ while Gautam argues that they are usually C₁₈ and higher [25,31]. Nevertheless, these are higher molecular weight hydrocarbons. The most common method for measuring these components is to

pass a diluted sample through a particulate filter (as specified in the Federal Test Procedure) and then through a trap containing XAD-2 adsorbent (Figure 5). The particulate trap is processed to extract the soluble organic fraction (SOF). Usually this is done by soaking the filter in a Soxhlet apparatus using dichloromethane as the solvent. The amount of "soak time" can range from 6-24 hours. The mixture is then concentrated and analyzed using liquid chromatography. The SOC is removed and analyzed from the XAD-2 in the same manner described above using acetone as the solvent.

Westerholm discusses two other ways of sampling the SOC [32]. The first of these is a cryogenic technique in which the sample is trapped in a chilled sample tube packed with a sorbent bed. The second sampling technique is to use a plug of polyurethane foam to trap the SOC. The polyurethane foam method yielded results which were comparable to the XAD-2 resin samples; however, the cryogenic results were lower. As a result, the cryogenic technique is not recommended. While these represent common measurement techniques, there are other valid variations [33-35].

10.0 INSTRUMENT CALIBRATION

Due to the low vapor pressures associated with high molecular weight hydrocarbons, preparation of calibration gases is trivial. Since the typical hydrocarbon distribution for diesel fires is unknown, the instrument should be calibrated at a concentration close to the LEL for a range of possible hydrocarbons. For hydrocarbons such as nonane (C_9H_{20}) and decane ($C_{10}H_{22}$), an explosive mixture cannot be achieved at standard atmospheric conditions ($25^\circ C$, 760 torr). The LELs for nonane and decane are 0.83% and 0.77% by volume, respectively. For nonane, only a mixture of 35% of the LEL (or 0.3% by volume) can be prepared at standard conditions. For decane, a mixture corresponding to 29% of the LEL (or 0.22% by volume) can be prepared.

As a result, it would be necessary to either prepare a standard which is subatmospheric or at an elevated temperature (since the vapor pressure increases with increasing temperature).

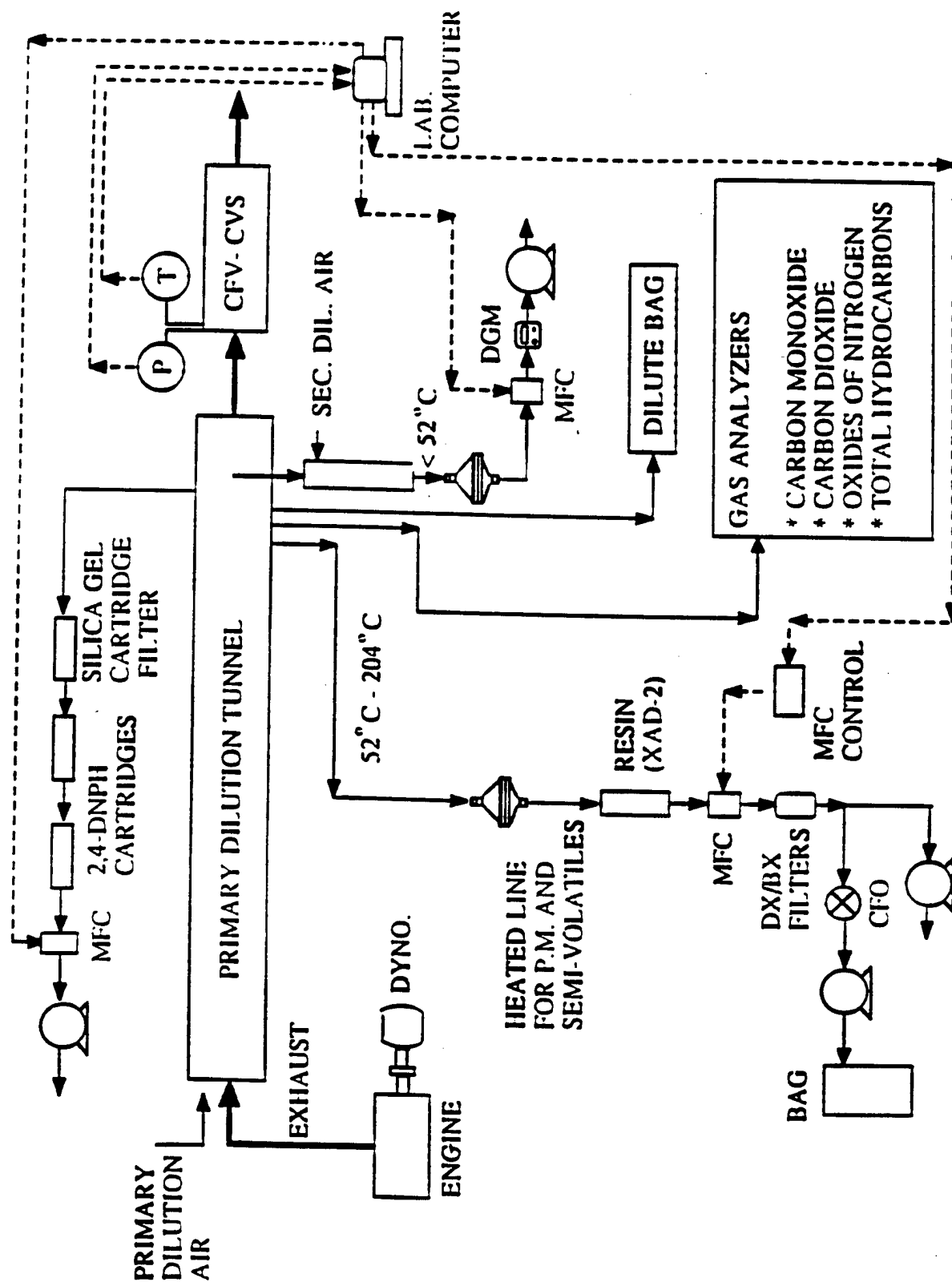


Fig. 5 - Typical schematic for particulate measurement (taken from Gautam et al. [25])

Subatmospheric mixtures need special care since a leaking container could allow ambient air to be drawn into the sample and thus dilute it. Preparing the standard at an elevated temperature would be troublesome since the container must be maintained at a specific temperature and be uniform.

As a guideline, some calculations were performed for decane to determine what conditions would be necessary to prepare a mixture which is 90% of the LEL (0.69% by volume). In order to avoid creating a subatmospheric sample, the temperature would need to be approximately 43°C. If the sample pressure is lowered, the sample could be prepared at 25°C if the total pressure is 246 torr.

These problems should be taken into consideration when planning for these measurements. If higher molecular weight hydrocarbon sampling is desired, it is important to calibrate the system properly.

11.0 SUMMARY AND RECOMMENDATIONS

There is a need to identify a hydrocarbon sensor for use on Navy surface ships and submarines in Class B fire scenarios. However, in order to properly validate a sensor for this type of use, reliable baseline HC measurements are needed for comparison purposes. In previous testing conducted onboard the *ex-USS SHADWELL*, significant problems with obtaining these baseline measurements were noted. As a result, this study examined different hydrocarbon measurement techniques and discussed their suitability for Class B fire scenarios. The objective of this was to provide recommendations which would improve the existing measurement technique.

Based on this study, it is concluded that the existing techniques used previously on the *ex-USS SHADWELL* are inadequate for measuring the hydrocarbon concentrations from Class B fires, such as spray fires. This study has clearly demonstrated the requirement that gas samples must either be heated or diluted; otherwise, hydrocarbons may condense out of the sample before they are measured.

It is important to note that the studies discussed above differ from this unique Class B fire application. In the automotive studies, the measured concentrations of hydrocarbons were much less than the lower explosive limit (LEL). Automotive researchers are struggling to measure hydrocarbons at the hundred ppm level to satisfy emissions regulations. In contrast, typical hydrocarbon LELs are on the order of 50,000 ppm C₁.

A review of previous fire research studies indicates that there is a significant amount of difficulty in making accurate hydrocarbon measurements in fire scenarios. Measurement errors were shown to increase with an increase in the global fuel-to-air ratio. In addition, large errors were noted for fuels which have much lower molecular weights than diesel fuel (i.e., hexane and toluene). These findings show that the fire scenario has a large impact on the quality of hydrocarbon measurements. There are three main scenarios which would be expected. In a well-ventilated fire, low concentrations of hydrocarbons would be expected and the primary species would be of low molecular weight. In contrast, a fire which was not well-ventilated would be expected to produce greater concentrations of hydrocarbons and partially oxidized hydrocarbons (i.e., higher molecular weight hydrocarbons). In the worst case, raw fuel may be present in the sample. This may not require the presence of a fire since an uncontrollable fuel leak could allow an explosive concentration of fuel aerosol to form. It would be expected that there would be a large variation in the measurement difficulties encountered with these three situations. This variation is due to such factors as the amount of particulates generated and the distribution of the hydrocarbons in the sample. Analysis of higher molecular weight hydrocarbons has been shown to be much more difficult than that of lower molecular weight hydrocarbons.

The test procedures which were described in this report are helpful for identifying a good measurement procedure. There are two separate elements needed for the final design, the sampling and the measurement technique; each will be discussed separately. Associated with these techniques are clear advantages and disadvantages. As a result, there is no combination of sample and measurement methods which will guarantee accurate measurements in the three scenarios described above.

The sampling methods described in Method 25 are complicated and require specifically designed components. There are numerous steps involved which yield only a total hydrocarbon measurement. In order to implement this technique in a fire scenario, either the sample probe would need to be very long or a substantial amount of equipment would need to be set up near the fire site. The technique of taking diluted samples as specified in the Federal Test Procedure is also questionable. First of all, in order to take a diluted sample from the fire space, a fresh, clean air or nitrogen supply would need to be collocated at the mixing point. A "tunnel" would need to be constructed and a method of determining the flow rates of the two components would be required. Furthermore, conflicting results have been documented pertaining to the losses that are associated with this technique. Jensen, et al., measured no significant losses in higher molecular weight hydrocarbons when comparing diluted gasoline and alternative fuel exhaust samples to non-diluted samples [17]. Lach, on the other hand, consistently measured HC concentrations 55-60% lower for diluted diesel exhaust samples than for undiluted samples [36]. The differences seen between these two studies may be due to the fuels used. This raises some uncertainty as to how representative the diluted sample concentrations are of the real concentrations. As a result, the use of diluted samples would require that a comparison between diluted and non-diluted samples be examined.

As for measurement techniques, the use of gas chromatography to analyze the samples would be time consuming and expensive. A speciated analysis of the sample would be interesting, but may not be necessary for this type of analysis. Since the use of FTIR methods has shown that identification of higher molecular weight compounds is problematic, it is not a viable option. The use of an FID has disadvantages as well. If the gas sample is drawn directly from the compartment and not diluted, the sample line should be as short as possible due to the heating requirements. This would require that the instrument be located near the fire source along with a supply of hydrogen and air for the FID flame. The use of an FID would yield total HC concentration measurements as compared to speciated concentration measurements. This type of measurement raises several issues. In order to calibrate the FID, a hydrocarbon that is "representative" of those in the sample should be used. In addition, because of significant uncertainty in the linearity of FID response with

respect to different molecular weight hydrocarbons, quantitative analysis may be suspect. Uncertainties as high as 25% have been reported.

Based on these advantages and disadvantages, there are two techniques that would be best suited for this Class B fire analysis. A GC/FID system (such as the system on the *ex-USS SHADWELL*) may be used with either an entirely heated sample system, or diluted samples. If the heated sample system option were incorporated, the sample would be collected in a heated container. This container would be kept heated in an oven until the time of analysis, and all components of the GC injection system would need to be heated. This design would ensure that the sample never cooled enough to condense a measurable concentration of hydrocarbons. If diluted samples were taken instead, a mini-dilution tunnel would be needed so that the exhaust sample could mix with the dilution air prior to sample collection. As mentioned in the previous paragraph, a comparison between diluted and undiluted sample measurements should be performed to ensure that diluted samples are truly representative of the actual concentrations.

Another option would be to use a hot FID. The analyzer would be located close to the test area and the sample lines would be heated to 200°C. A particulate filter would be needed in the sample line upstream of the FID. This filter should also be heated to 200°C to minimize the loss of hydrocarbons on it. Analysis of the particulate filter should be performed after initial tests to determine if a significant percentage of hydrocarbons was trapped onto it. This analysis would be performed using the methods presented in Section 9 and analyzed using either high precision liquid chromatography or gas chromatography, depending on the extraction method. This process would need to be repeated until there is better knowledge of the hydrocarbons that are lost on the filter. It may ultimately be determined that this analysis is not necessary, particularly for samples which have low concentrations of high molecular weight hydrocarbons.

The use of a hot FID, located close to the sample point, would be more advantageous than the GC/FID. A hot FID system would be the easiest to implement, and the prospect of completely measuring the higher molecular weight hydrocarbons would be greater. Furthermore, in order to

verify the diluted samples associated with GC/FID analysis, the heated sampling system needed for the FID setup would be required.

The implementation of any measurement technique would require that the instrument be calibrated with a wide range of hydrocarbons and concentrations. This would be an intensive process especially for fire tests in which parent fuel may be present. In order to validate a combustible gas meter, concentrations covering at least 0 to 75 % of the LEL would need to be verified. As discussed in Section 10, calibration mixtures containing higher molecular weight hydrocarbons (i.e., greater than C_8) at concentrations approaching the LEL cannot be prepared at ambient conditions. Consequently, it is recommended that these standards be prepared by placing a sample container inside of an oven with precise temperature control. The sample container would remain in the oven at all times. In order to analyze the mixture, a heated sample line should be installed directly into the sample inlet of the instrument. It would be critical that the temperature of the line also be precisely controlled since a temperature drop could cause some percentage of the hydrocarbons to condense thus changing the concentration of the mixture. Care should be exercised if standards approaching the LEL are prepared in air at elevated temperatures. Nitrogen would be a better choice of diluent. An alternative to this technique would be to prepare a subatmospheric standard; however, this would require high precision equipment. Also, there is a risk of sample dilution that could be caused by a leak in the sample container.

There are no published studies which indicate that researchers have been successful at solving this problem. As a result, it is uncertain how effectively any of these techniques will measure hydrocarbon concentrations in Class B fire scenarios, particularly those scenarios in which parent fuel may be present. It is clear that a substantial amount of work would be required to make these measurements, not only to set up a new or improved system, but also to perform all the verifications necessary to ensure that the measurements are meaningful.

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